Indian J. Phys. **51B**, 184-188 (1977)

Geometry of benzaldehyde molecule in the first triplet excited state

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1. INTRODUCTION

The rotational analysis of an electronic transition involving a triplet and a singlet state is a very complicated affair especially with regard to the intensity distribution in the rotational structure. Several theoretical discussions of the topic are available in literature (1, 2) but their application to the analysis is very limited (3, 4, 5) because of very heavy and difficult computations involved. There are favourable cases, however, in which a triplet–singlet transition will have only one component of the transition moment contributing prominently and the resulting structure may resemble that of a singlet-singlet electronic transition. The triplet-singlet electronic emission of benzaldehyde seems to be a special case in which the observed rotational contour looks very similar to that of a singlet-singlet electronic transition.

2. EXPERIMENTAL

The emission spectrum was recorded in the first order of an f/8.4, 1-meter Spex spectrograps. The experimental details are given in an earlier paper (6). The observed rotational band contour for the O°_{0} band of triplet-singlet emission is shown in figure 1(a).

Rotational selection rules for symmetric and near symmetric rotor molecule :

A triplet-singlet transition is made allowed by mixing some singlet character into the triplet state or some triplet character into the singlet state. Such mixing is caused by spin-orbit interaction. Suppose the symmetry of upper vibronic state is $^{3}\Gamma_{T}$ and that of the lower state is $^{1}\Gamma_{s}$. Hougen[1] has shown that there will be two possible kinds of singlet-triplet transitions in a molecule of symmetry Cs one corresponding to $^{3}\Gamma_{T} \times {}^{1}\Gamma_{s} = A'$ and the other corresponding to $^{3}\Gamma_{T} \times {}^{1}\Gamma_{s} = A''$. If we assume Hunds case(b) for the coupling of various angular momenta in a polyatomic molecule then each rotational state will be characterized by four quantum numbers for a symmetric rotor molecule.

J = total angular momentum including spin
P = component of J along the symmetry axis,
N = total angular momentum of molecule excluding spin,
K = component of N along the symmetry axis.

In the theory used for the present computations K, N and J are good quantum numbers but not P. The general selection rules on these quantum numbers for triplet-singlet electric dipole transitions in symmetric rotor molecules are

$$\Delta J = 0, \pm 1$$
$$\Delta N = 0, \pm 1, \pm 2$$
$$\Delta K = 0, \pm 1, \pm 2$$

3. Computation of Rotational Band Contours

Benzaldehyde is a near prolate symmetric rotor with asymmetry parameter $k = -0.82$ and it belongs to C_s symmetry. To compute singlet-singlet transitions one will have to apply different set of selection rules depending on

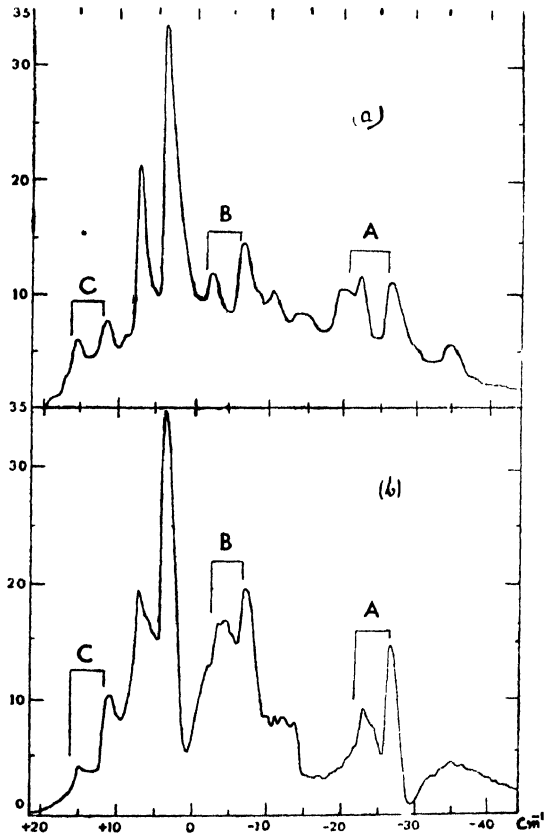

Fig. 1a. Observed rotational band contour of O°_{0} band of triplet-singlet emission of benzaldehyde.

Fig. 1b. Computed type B contour of benzaldehyde with sequences added The intensities in the sequence bands are A(0.50), B(0.50) and C(0.35) where quantities within brackets represent the ratio of sequence band intensity to the main band intensity.

the fact that the transition moment lies in the plane of the molecule or perpendicular to the plane of the molecule. We have chosen the molecule fixed z-axis to be along the carbon-substituent bond and x-axis perpendicular to the molecular plane. For in-plane transition the band will have a type-A-type B hybrid character whereas for transition moment perpendicular to molecular plane the band will be type C. It is essential to know the three rotational constants for the lower and the upper electronic states for computation of rotational contour of the band. The rotational constants for the ground state are available from microwave spectrum of benzaldehyde[7] and are included in table 1. The first trial set of excited state rotational constants were obtained from the following procedure.

1. Geometry of the carbon ring was assumed to be that of the $^1B_{2u}$ state in benzene in which C—C = 1.43 A and C—H = 1.07 A the bond angles remaining unchanged[10]
2. The value of C-O bond length was obtained from a knowledge of the C=O stretching frequency in the ground state (1728 cm^{-1}) and that in the excited, state (1368 cm^{-1}. The relation $r' = r''\ (\omega''/\omega')^{1/2}$ was used as in diatomic molecules to obtain $r' = 1.356$ A.
3. The value of C-CHO bond was obtained from a relation used in step[2] and taking
   $\omega'' = 1204\ cm^{-1}$, $\omega' = 1314\ cm^{-1}$ (See 6, 8, 9)

Thus giving C-CHO = 1.42 A.

The C-H bond in the aldehyde group was assumed to be unchanged.

Table 1. Rotational constants for benzaldehyde

Ground $^1A'$ State	Excited $^3A''$ State	
$A'' = 0.17467t\ cm^{-1}$	$A' = 0.170056\ cm^{-1}$	$A = -0.00462 \pm 0.0001$*
$B'' = 0.052236\ cm^{-1}$	$B' = 0.052236\ cm^{-1}$	
$O'' = 0.040211\ cm^{-1}$	$C' = 0.039961\ cm^{-1}$	$C = -0.00025 \pm 0.00001$
$K'' = -0.82$	$K' = -0.81$	

*These uncertainties are determined from deviations in rotational features of the computed contour.

Table 2. Geometry of benzaldehyde molecule in $^3A''$ state

Model	A'(cm^{-1})	B'(cm^{-1})	C'(cm^{-1})
Model-1			
C–C ring = 1.435A C–CHO = 1.380A C=O = 1.311A	0.166018	0.051930	0.039557
Model-2			
C–C ring = 1.416Å	0.169780	0.052705	0.040220

These rotational constants were used to compute the first set of type A, type B and type C rotational contours using a computer program described earlier[11]. It was found that only type B rotational contours showed some resemblance to the observed contour of the electronic 0-0 band of benzaldehyde figure 1(a). The excited state rotational constants were modified to obtain the best fit between the observed and computed rotational band contour. The type A and type B rotational contours using the best set of excited state rotational constants are given in figure 2(a) and 2(b) respectively. In these

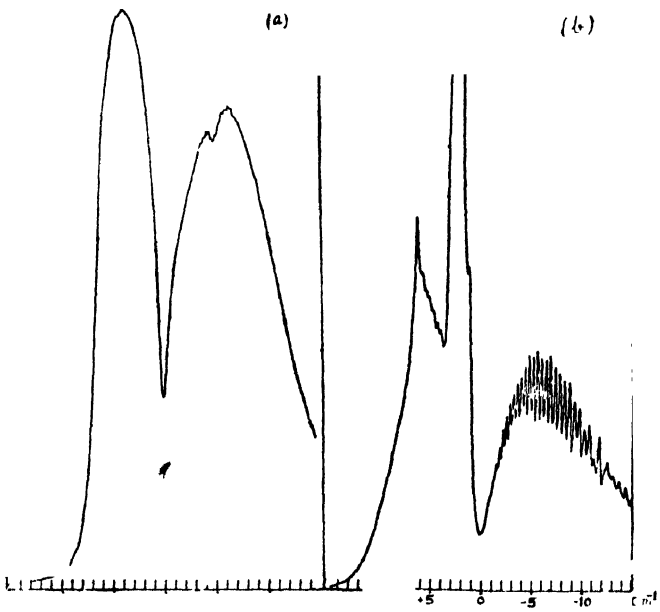

Fig 2a. Computed type A rotational band contour using rotational constants given in table 1.

Fig. 2b. Computed type B rotational band contour.

computations the maximum value of N was 150 and symmetric rotor approximation was used for rotational levels with $K > 40$. The computed intensities were plotted and a triangular broadening function was used to produce a half intensity line width of 0.1 cm^{-1}. It was found that a hybrid type A-type B band contour did not improve resemblance between the observed and computed rotational contours.

4. Geometry Calculations

The excited state rotational constants reported in table-1 have been obtained on the assumption that molecule remains planar in this excited state. Thus there are only two independent data for calculating several bond lengths

and bond angles which is impossible unless one makes some simplifying assumptions. Our first attempt was to assume excited state geometry for the carbon ring to be that of benzene in its $^1B_{2u}$ state and the C=O and C-CHO bonds were varied to reproduce the observed excited state constants. The best results using the assumptions are summarized in table-2 we call this model 1. The best agreement between the observed and computed rotational constants, was obtained when the geometry of the carbon ring was changed slightly from that in Model 1 keeping the C=O and C-CHO bonds the same as in model 1. We call this model 2.

It can be seen that both models 1 and 2 are consistent in the fact that they predict an expansion of carbon ring, a contraction of C-CHO and an increase in C=O bond in going from singlet to the triplet state. These facts are qualitatively supported by a long progression in C=O stretching vibration and smaller ones in C-CHO stretching and carbon ring breathing vibrations.

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